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DIURNAL VARIABILITY OF $\delta^{13}\text{C}$ AND $\delta^{18}\text{O}$ OF ATMOSPHERIC CO_2 IN THE URBAN ATMOSPHERE OF KRAKÓW, POLAND

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This article presents the results of measurements of the isotopic composition and concentration of atmospheric carbon dioxide, performed on air samples from Kraków (Southern Poland) in different seasons of the year. A simple isotope mass balance model has been applied to determine the contributions of different sources of CO_2 to the urban atmosphere of Kraków city: the latitudinal/regional background, biospheric contributions and anthropogenic emissions. The calculations show that during the summer and early autumn the dominant contribution to local CO_2 peaks is the biosphere, making up to 20% of atmospheric CO_2 during the nocturnal temperature inversion in the lower troposphere. During early spring and winter, anthropogenic emissions are the main local source.

Keywords: Anthropogenic emission; Carbon 13; Carbon dioxide; Global change; Oxygen 18

INTRODUCTION

A better understanding of the processes accompanying the transport of carbon in the global atmosphere–biosphere–ocean ecosystem is an important issue in the light of possible climatic consequences of large anthropogenic emissions of carbon dioxide into the atmosphere. The isotopic composition of carbon and oxygen in atmospheric CO_2 can help to quantify sources and sinks of CO_2 , both on regional and global scales [*e.g.* Refs. 1–4]. Isotopic investigations of atmospheric CO_2 can be particularly useful when studying the carbon cycle in heavily polluted urban areas, with high input of carbon dioxide from burning of fossil fuels (heating, car traffic) and from industrial activities [5] as well as the role of the biosphere in global carbon cycle [6].

Kraków is a large urban centre with more than 800,000 inhabitants, located in the south of Poland (500°N, 200°E, 220°m asl.). The city is housing a large steel factory as well as

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numerous other industries. Characteristic for the town is an old-fashioned house heating system (single room ovens running on coal), still in operation in numerous houses in the centre of the city. This results in intensive emissions of CO₂ from low-temperature and thus low-quality combustion during the winter period. Heavy car traffic is another factor contributing to the pollutant load of the local atmosphere. In addition, the most industrialised region of Poland (Silesian District), with heavy industry, coal mining and high population density is located approximately 100 km west of the city. Thus, with prevailing westerly circulation, Kraków is often under the influence of air masses crossing the Silesian District, affected by high surface emissions of CO₂ and methane. The location of the town in a river valley, surrounded by hills, results in a relatively frequent occurrence of strong night-time inversion situations, particularly during wintertime.

In this article, we present and discuss five series of measurements of diurnal variability of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of near-ground atmospheric CO₂ collected in Krakow at four different seasons of a year. In all cases, basic meteorological data were recorded (surface air temperature, relative humidity, atmospheric pressure), back trajectories were calculated at a 6-h time resolution [7], and in the samples of the last diurnal cycle the CO₂ concentration was also measured.

EXPERIMENTAL

The sampling site was situated at the faculty building of the University campus, with the air intake being located on the roof about 20 m above ground level, in the western part of the city, bordering recreation and sports grounds. Neither direct low-emission sources nor strong car traffic exist nearby the sampling site. The air was pumped from the roof to the laboratory through about 15 m PTFE tubing of 2 cm diameter, and directly introduced into the glass vacuum line at 0.2 l/min. The time lag between the air inlet and vacuum line was ca. 2 min. Water vapour and CO₂ were removed from the air stream using glass cold traps in dry ice/alcohol and liquid nitrogen, respectively. The sample size was fixed to 10 l of air in order to provide enough CO₂ for mass spectrometry (0.15 mmol). Each sample was collected during 50 min, representing the mean value for the collection period. The extraction method had been checked prior to the experiments for fractionation effects associated with the extraction, with respect to both carbon and oxygen isotopes. They appeared to be smaller than 0.1‰ for both isotopes at flow rates below 0.2 l/min. These pure CO₂ samples were measured in Kraków, using a Micromass VG 602 mass spectrometer (MS). The last experiment was performed in 1994. During this experiment, a different sample preparation method was applied. The samples were collected in 1 l glass flasks by flushing them with air sucked from the roof of the faculty building into the laboratory. The air was dried by means of magnesium perchlorate (Mg(ClO₄)₂). The amount of flushed air exceeded 10 times the flask volume to avoid contamination by the air stored in the flasks before filling. Before filling, the flasks have been flushed with dry nitrogen while being heated to 300 °C, to remove any water vapour adsorbed on the inner surfaces. Subsequently, the flasks were flushed and filled again with dried ambient air (dew point < -50 °C) to establish an equilibrium between the air and the surfaces at atmospheric concentration levels for all trace gasses. The measurements on these flasks were carried out in Heidelberg. The CO₂ concentration was determined by gas chromatography [8]. The stable isotope composition of carbon and oxygen in CO₂ was measured on a Finnigan MAT-252 MS equipped with an online MT-box system for freezing CO₂ out of an aliquot (around 0.1 l) of the air sample dynamically and automatically. All isotope results are given on the international standard VPDB for $\delta^{13}\text{C}$ and VPDB-CO₂ for $\delta^{18}\text{O}$ [9]. The results of experiment done in 1994 were also corrected for isobaric N₂O-contributions [10].

RESULTS AND DISCUSSION

Five sampling campaigns were performed in different seasons as examples for diurnal changes of isotope characteristics of atmospheric CO_2 during contrasting seasonal conditions. The basic meteorologic parameters were monitored during the experiments. The obtained data reveal distinct diurnal variability, both for the isotopic composition and the concentration of carbon dioxide. A strong anti-correlation between temperature, relative humidity, concentration and isotopic composition of CO_2 was observed while no correlation exists between atmospheric pressure and isotope parameters. That means that the changes of the atmospheric pressure did not induce substantial changes of the local CO_2 fluxes. An example of a meteorological record is shown in Figure 1(A)–(C). The anti-correlation between temperature and relative humidity is clear and means that no significant change in the absolute water vapour content was observed, suggesting that no air mass change occurred during the sampling period. In addition, the calculated back trajectories show that in most cases the air circulation was stable during the experiments. However, during one of the experiments (July 1992), the origin of the five-day back trajectory moves from Italy to the North polar region between Svalbard and Greenland. The consequences of this large change are clearly visible in the data and will be discussed later (Fig. 2). Stable conditions are important with respect to fulfilling the assumptions of the model described in the next section. The isotope values are correlated with the temperature, because the temperature change is responsible for the creation of a night-time inversion layer. The existence of an inversion layer induces the accumulation of CO_2 emitted from local sources in the lower troposphere during the night and is observed as increase of its concentration and decrease of the isotopic composition (emitted CO_2 has more negative delta values than free atmosphere). The first four experiments were performed during spring, summer and winter of 1992. The results are summarised in Figure 3(A)–(D). The last sampling campaign

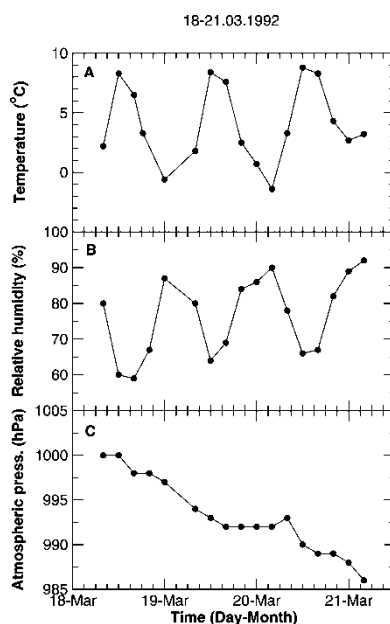


FIGURE 1 The example of meteorologic data record for the experiment done 18–21 March 1992 (big ticks at midnight).

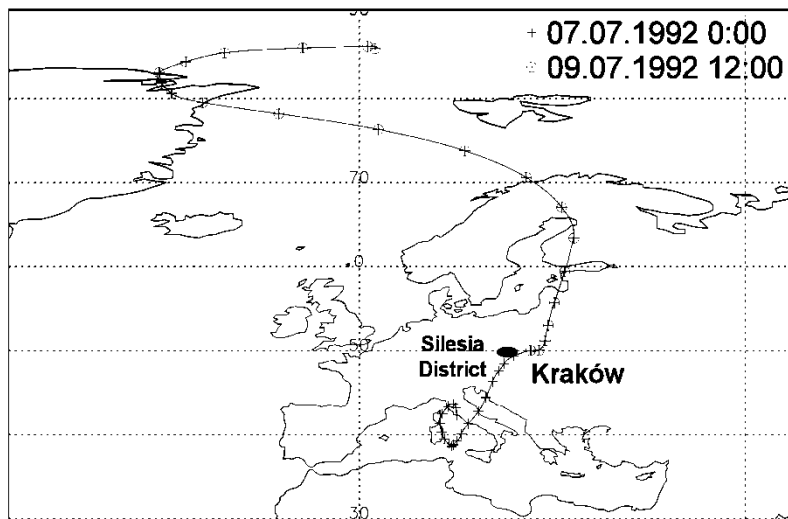


FIGURE 2 The example of back trajectories calculations for the period 7–10 July 1992. All trajectories ending at Kraków, going backwards in time by 6 h per tick.

was performed in September 1994. This time, in addition to isotope analyses, the CO_2 concentration was measured. The results are shown in Figure 4(A) and (B).

The highest concentrations of CO_2 were observed during the night (up to 440 ppm), when a strong temperature inversion was occurring. The accompanying isotope values ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) turned out to be the most negative (as low as -11.5‰ and -3‰ , respectively), suggesting that the local source of CO_2 during the night is characterised by more negative delta values than the background CO_2 for both elements. During the daytime, when the lower atmosphere was intensely mixed, the recorded CO_2 concentration dropped to values close to those observed at ‘clean’ continental stations (354 ppm at NOAA-station Baltic Sea). In addition, the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values were approaching those being characteristic for background CO_2 (around -7.80‰ and -1.2‰ , respectively [11]).

It should be noted that in all five experiments, the variations of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of atmospheric CO_2 were strongly correlated. Figure 5(A)–(D) shows the best linear fit lines for the correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. An interesting case is observed during the first of the experiments performed in July 1992 (Fig. 5(B)). Here, the data clearly can be splitted into two parts with different slopes of the linear regression lines (circles – rainy period, squares – sunny period). This fact can be explained by a drastic change in the respective contributions of anthropogenic and biogenic CO_2 . This coincided with rainfall, which took place at the beginning of the sampling period and a change of air mass circulation observed at back trajectories plots. Rainfall influences the soil–atmosphere CO_2 -exchange in two ways: it closes pores in the soil reducing the CO_2 flux to the atmosphere and may change the actual isotopic ^{18}O -equilibrium between soil CO_2 and soil water by increase of the time of equilibration and by change of the isotopic composition of soil water.

Model Calculations

The carbon isotope composition of atmospheric carbon dioxide in studies of the local balance of CO_2 is commonly interpreted using a simple, two-component mixing model [12]. It is assumed in this approach that atmospheric CO_2 near the ground level (c_{tot})

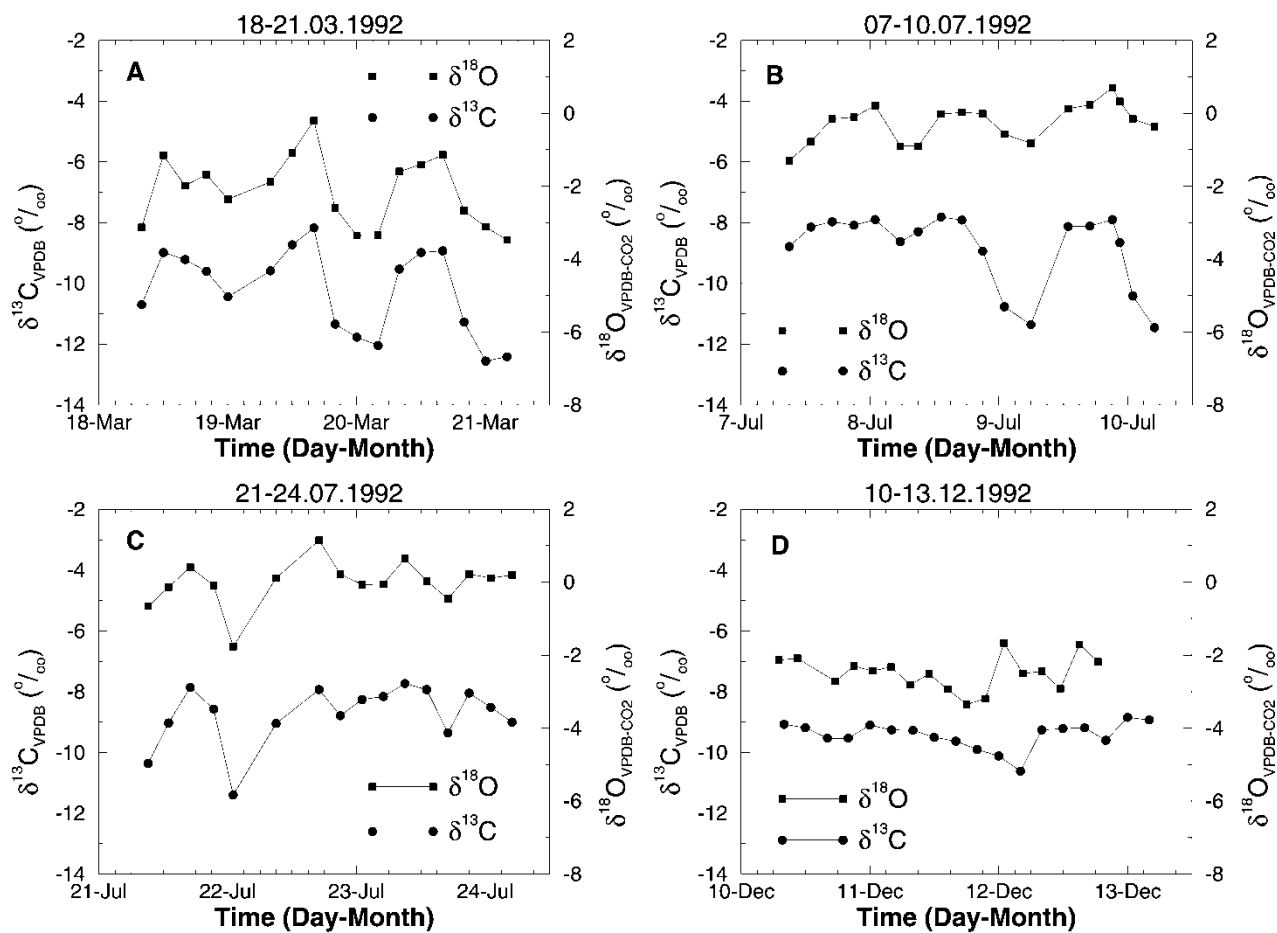


FIGURE 3 The isotopic composition of atmospheric carbon dioxide (March, July and December 1992).

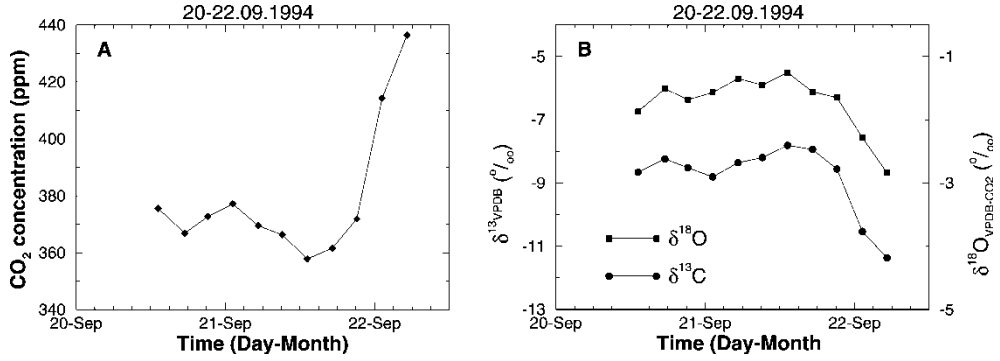


FIGURE 4 The concentration and isotopic composition of atmospheric carbon dioxide (September 1994).

consists of two components, characterised by distinct isotope δ -values: the background, 'free troposphere' CO₂ (c_{bg}) and the 'local' CO₂ originating from surface emission(s) (c_{src}) in the study area.

$$c_{tot} = c_{bg} + C_{src}, \quad (1)$$

$$c_{tot} \delta^{13}C_{tot} = c_{bg} \delta^{13}C_{bg} + c_{src} \delta^{13}C_{src}, \quad (2)$$

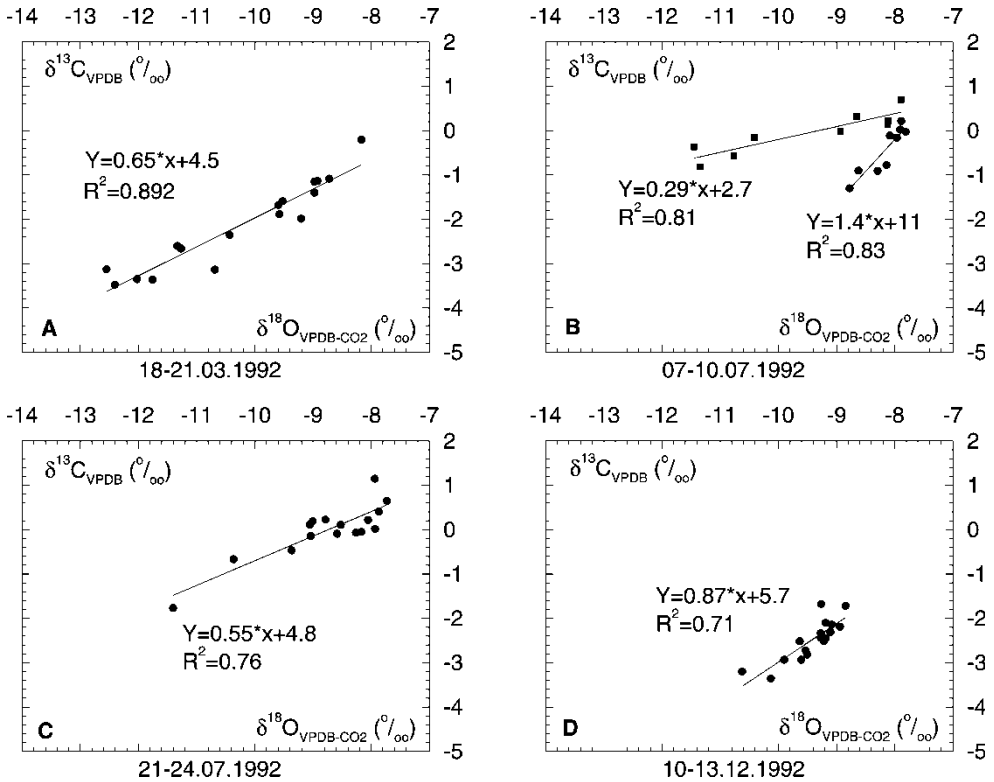


FIGURE 5 Correlation between $\delta^{13}C$ and $\delta^{18}O$ of atmospheric carbon dioxide.

where C_{tot} , $\delta^{13}\text{C}_{\text{tot}}$ are the measured concentration and isotopic composition of atmospheric CO_2 collected near the ground level; c_{bg} , $\delta^{13}\text{C}_{\text{bg}}$ are the concentration and carbon isotopic composition of 'free troposphere' CO_2 and c_{src} , $\delta^{13}\text{C}_{\text{src}}$ are the concentration and carbon isotope composition of 'local' CO_2 ;

From such a model one can calculate the isotopic composition of the mean local source of CO_2 , using the relationship derived from the isotope mass balance approach:

$$\delta^{13}\text{C}_{\text{tot}} = c_{\text{bg}}(\delta^{13}\text{C}_{\text{bg}} - \delta^{13}\text{C}_{\text{src}}) \frac{1}{c_{\text{tot}}} + \delta^{13}\text{C}_{\text{src}}. \quad (3)$$

The intercept of the best linear fit line approximating the $\delta^{13}\text{C}$ values as a function of $1/c$ will be interpreted in the framework of such a model as the isotopic composition of the mean local source of CO_2 . This model works well for carbon isotopes. However, it cannot distinguish very well between anthropogenic and biogenic sources of CO_2 because the $\delta^{13}\text{C}$ values of biogenic and anthropogenic carbon dioxide are very similar (ca -26%) [13].

In the case of $\delta^{18}\text{O}$, the situation is more complicated. The difference between biogenic and anthropogenic CO_2 is variable and can be large under certain circumstances. The $\delta^{18}\text{O}$ values of anthropogenic CO_2 fluctuate around -17% [14], whereas the values of biogenic CO_2 vary from -12% to $+8\%$ [15–17]. It is important to stress here that changes in the carbon isotopic composition are always related to fractionating uptake or release processes of CO_2 , whereas the oxygen isotopic fingerprint of CO_2 is easily altered by isotopic exchange with water, without physically moving CO_2 to another reservoir. In this case, the Keeling-type two-component mixing model will become obsolete. Farenzy and Tans [18] first suggested the potential influence of the land biosphere on the $\delta^{18}\text{O}$ of global atmospheric CO_2 by isotope exchange with leaf water. In addition, isotope exchange processes between CO_2 and surface water bodies can locally modify the $\delta^{18}\text{O}$ values of CO_2 in relatively short time (a few hours) [19].

The approach proposed here to interpret ^{13}C and ^{18}O isotope data for local CO_2 is based on a three-component mixing model. We assume that the local atmospheric CO_2 near the ground level (c_{tot}) consists of three components: background CO_2 representing the regional atmosphere not influenced by local sources of carbon dioxide (c_{bg}), the local biogenic component representing contributions from the biosphere (c_{bio}) (decay of organic matter and root respiration, but also CO_2 -uptake by photosynthesis) and the local anthropogenic component (c_{ant}) (car traffic, domestic heating systems, industrial emissions). The following isotope-mass balance equations can be formulated:

$$c_{\text{tot}} = c_{\text{bg}} + c_{\text{bio}} + c_{\text{ant}}, \quad (4)$$

$$c_{\text{tot}}\delta^{13}\text{C}_{\text{tot}} = c_{\text{bg}}\delta^{13}\text{C}_{\text{bg}} + c_{\text{bio}}\delta^{13}\text{C}_{\text{bio}} + c_{\text{ant}}\delta^{13}\text{C}_{\text{ant}}, \quad (5)$$

$$c_{\text{tot}}\delta^{18}\text{O}_{\text{tot}} = c_{\text{bg}}\delta^{18}\text{O}_{\text{bg}} + c_{\text{bio}}\delta^{18}\text{O}_{\text{bio}} + c_{\text{ant}}\delta^{18}\text{O}_{\text{ant}}, \quad (6)$$

where c_{tot} , $\delta^{13}\text{C}_{\text{tot}}$, $\delta^{18}\text{O}_{\text{tot}}$ are the measured concentration and isotopic composition of atmospheric CO_2 collected near the ground level; $\delta^{13}\text{C}_{\text{bg}}$, $\delta^{13}\text{C}_{\text{bio}}$, $\delta^{13}\text{C}_{\text{ant}}$ are the carbon isotopic composition of the respective components of atmospheric CO_2 ; $\delta^{18}\text{O}_{\text{bg}}$, $\delta^{18}\text{O}_{\text{bio}}$, $\delta^{18}\text{O}_{\text{ant}}$ are the oxygen isotopic composition of the respective components of atmospheric CO_2 and c_{bg} , c_{bio} , c_{ant} the calculated concentration of the respective components of atmospheric CO_2 .

The isotope-mass balance equations can be solved for selected time intervals for the required set of variables (*e.g.* c_{bg} , c_{bio} and c_{ant}), provided that the isotopic composition of individual components is constant during the selected time interval and the corresponding

values are known or can be assessed. The adopted three-component mixing model also requires that the observed changes of concentration and isotope composition of atmospheric CO₂ are exclusively due to varying mixing conditions and/or changes in local CO₂ fluxes. The model approach cannot be applied, *e.g.* during air mass changes (see below).

The sensitivity of the adopted model was tested for two points selected from the diurnal cycle data set collected in September 1994. They represent two contrasting conditions: relatively low CO₂ levels (day time, vigorous vertical mixing, intense anthropogenic emissions) and relatively high CO₂ levels (night, absence of assimilation, build-up of biogenic CO₂). The calculations revealed that the calculated components of the atmospheric CO₂ concentration are most sensitive to changes of the isotopic composition of the background CO₂ (~50 ppm/‰) for both isotopes, which in any case will constitute the largest contribution at all. For other components, the sensitivity of the model was less than 10 ppm/‰. Inversely, the changes in the $\delta^{18}\text{O}_{\text{bio}}$ value introduce only very small changes in the calculated concentrations. The explanation is the following: during the night, when the biogenic flux is dominant, assimilation is absent and the oxygen isotope composition reflects soil water values (plus temperature-dependent fractionation factors). During the day, the assimilation process causes a large ^{18}O isotope fractionation effect, but the (possibly negative!) contribution of biogenic CO₂ in the atmosphere on the ^{18}O is negligible in this study. The conclusion is that this model cannot be used for long time periods when the background conditions are varying with time.

The three-component mixing model was applied for the data set collected during September 1994. Apart from the measured values (concentration and isotopic composition of atmospheric CO₂), the following assumptions were made: (i) the isotope composition of individual components is constant during the experiment, (ii) changes of concentration and isotope composition are due to changes in atmospheric mixing conditions or changes in local CO₂ fluxes. Equations (4)–(6) were solved for each air sample. The isotopic composition of individual components ($\delta^{13}\text{C}_{\text{bg}}$, $\delta^{13}\text{C}_{\text{bio}}$, $\delta^{13}\text{C}_{\text{ant}}$, $\delta^{18}\text{O}_{\text{bg}}$, $\delta^{18}\text{O}_{\text{ant}}$) were assumed to be constant for all points. In case of $\delta^{18}\text{O}_{\text{bio}}$, such an assumption is hardly to be fulfilled (see below). The background isotope data were fixed using data of carbon dioxide measurements from the stations Baltic Sea and Hungary [11], to -7.6‰ for carbon and -1.2‰ for oxygen. The delta values for the mean anthropogenic component were derived from stable isotope measurements of CO₂ collected directly from exhaust products of the combustion sources (car engines, low and high emission, methane combustion) as -25‰ for carbon and -18‰ for oxygen [7]. The isotopic composition of the biogenic component was adopted from literature [16, 19, 20]. The $\delta^{13}\text{C}_{\text{bio}}$ value was set to -28‰ and $\delta^{18}\text{O}_{\text{bio}}$ between -10‰ and 0‰ , depending on the sampling time. For the night time, when no assimilation occurs -10‰ was applied reflecting the isotope composition of soil water. During the day 0‰ represents the influence of CO₂–water exchange in the leaves when assimilation exists. During sunrise and sunset a value of -5‰ was used. The results of the model calculations are shown in Figure 6. The meteorological conditions were stable during the experiment. There was no strong wind (wind speed was not measured but observed) and no rain.

The calculated background concentration is practically constant and equal to 355 ppm. This value agrees very well with the measurements carried out during the same period at the station Kasprowy Wierch located in the Tatra Mountains, approximately 100 km to the south of Kraków [21] and the station located on the Baltic Sea [11]. These two stations are relatively free of local influences and therefore should properly reflect the regional background concentration of CO₂. Further, it is apparent that the biogenic component as a source is dominating during the night, whereas the anthropogenic component prevails during the day. This is in agreement with the different nature of the two sources: biogenic CO₂ is released from the soil and vegetation at a constant rate. It accumulates in the lower

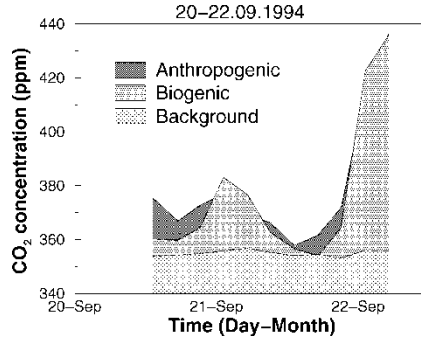


FIGURE 6 Model calculations of contribution of the background, biogenic and anthropogenic sources to atmospheric carbon dioxide concentration (September 1994).

atmosphere during the night when the assimilation process is absent and vertical mixing of the atmosphere is weak. During the day anthropogenic emissions dominate (car traffic, heating, industry, etc.). The biogenic flux is reduced by the assimilation process. In the studied period, the maximum contribution was calculated to 80 and 15 ppm for the biogenic and anthropogenic components, respectively (Fig. 6).

The data sets collected in 1992 (Fig. 3) were limited only to isotope analyses of carbon dioxide. It is obvious that in such cases Eqs. (4)–(6) cannot be applied directly. However, it is still possible to draw some conclusions with respect to the relative proportion of the biogenic and anthropogenic component in the near-ground atmospheric CO_2 , if we can assume that the background concentration is constant during the considered period. This is normally the case if we consider short periods of time (one or two days). If we express the biogenic (b) and anthropogenic (a) component as a fraction of the background CO_2 concentration, the following isotope mass balance equations can be formulated:

$$(1 + a + b)\delta^{13}\text{C}_{\text{tot}} = \delta^{13}\text{C}_{\text{bg}} + a\delta^{13}\text{C}_{\text{ant}} + b\delta^{13}\text{C}_{\text{bio}}, \quad (7)$$

$$(1 + a + b)\delta^{18}\text{O}_{\text{tot}} = \delta^{18}\text{O}_{\text{bg}} + a\delta^{18}\text{O}_{\text{ant}} + b\delta^{18}\text{O}_{\text{bio}}, \quad (8)$$

where a is the anthropogenic component of the total CO_2 concentration, expressed as a fraction of the background CO_2 concentration, and b is the biogenic component of the total CO_2 concentration, expressed as a fraction of the background CO_2 concentration.

For the interpretation of the data sets without CO_2 concentration values, the $\delta^{13}\text{C}$ values for each measuring event from 1992 were plotted against the corresponding $\delta^{18}\text{O}$ data (Fig. 5). On the basis of this data, the regression coefficients (A) from the correlation of the carbon and oxygen isotope values were derived. This coefficient can be described with Eqs. (7) and (8), which allows the derivation of Eq. (10):

$$A = \frac{\delta^{18}\text{O}_{\text{tot}} - \delta^{18}\text{O}_{\text{bg}}}{\delta^{13}\text{C}_{\text{tot}} - \delta^{13}\text{C}_{\text{bg}}}, \quad (9)$$

$$A = \frac{(a/b)(\delta^{18}\text{O}_{\text{ant}} - \delta^{18}\text{O}_{\text{bg}}) + (\delta^{18}\text{O}_{\text{bio}} - \delta^{18}\text{O}_{\text{bg}})}{(a/b)(\delta^{13}\text{C}_{\text{ant}} - \delta^{13}\text{C}_{\text{bg}}) + (\delta^{13}\text{C}_{\text{bio}} - \delta^{13}\text{C}_{\text{bg}})}, \quad (10)$$

In situations when 100% of the local CO₂ contribution is of biogenic origin, the slope A_{bio} of the linear fit of the ¹⁸O and ¹³C data (two-component mixing) can be expressed by the following equation:

$$A_{\text{bio}} = \frac{\delta^{18}\text{O}_{\text{bio}} - \delta^{18}\text{O}_{\text{bg}}}{\delta^{13}\text{C}_{\text{bio}} - \delta^{13}\text{C}_{\text{bg}}}, \quad (11)$$

where values with subscript 'bio' and 'bg' represent the measured (assessed) isotopic composition of the local biogenic CO₂ and background CO₂, respectively. If the contribution is solely of anthropogenic origin, the corresponding equation for A_{ant} will have the following form:

$$A_{\text{ant}} = \frac{\delta^{18}\text{O}_{\text{ant}} - \delta^{18}\text{O}_{\text{bg}}}{\delta^{13}\text{C}_{\text{ant}} - \delta^{13}\text{C}_{\text{bg}}}, \quad (12)$$

where values with subscript 'ant' and 'bg' represent the measured (assessed) isotopic composition of the local anthropogenic CO₂ and background CO₂, respectively.

Combining Eqs. (10)–(12), one can obtain the following expression for the ratio a/b representing the relative proportion of the anthropogenic to biogenic component in the sampled atmospheric CO₂. A detailed description of the development of the equations is given in an Appendix.

$$\frac{a}{b} = \frac{A_{\text{bio}} - A}{A - A_{\text{ant}}} \frac{\delta^{13}\text{C}_{\text{bio}} - \delta^{13}\text{C}_{\text{bg}}}{\delta^{13}\text{C}_{\text{ant}} - \delta^{13}\text{C}_{\text{bg}}}. \quad (13)$$

The slope (A) derived from the measured data was the basis to calculate the anthropogenic and biogenic component in the sampled CO₂. This ratio a/b was calculated for four diurnal cycles measured in 1992. The results are presented in Table I.

It is apparent from Table I that the ratio a/b is changing seasonally and that a higher value of A coefficient corresponds to air containing more anthropogenic CO₂. During early spring the biospheric activity is small and the anthropogenic contribution was larger than the biospheric one in that period. During summer time, the biospheric CO₂ is dominant introducing up to 90% of CO₂ to the atmosphere. During winter the local CO₂ contribution is made up almost exclusively from anthropogenic emissions. The ratio a/b presented for the experiment done in July 7–10 is calculated using the data from the second part (July 9–10) because during the first two days air masses were coming in from southern Europe (Fig. 2) and the background data assumed from Baltic Sea measurements lead to wrong results ($a/b < 0$). Unfortunately, background data from Hungary are not available for that period.

TABLE I The results of calculations of the a/b ratio.

Date	A	a/b
18–21.03.1992	0.65	1.19
07–10.07.1992 (second part)	0.29	0.06
21–24.07.1992	0.55	0.73
10–13.12.1992	0.87	6.15

TABLE II The comparison of model calculations and measurements of atmospheric CO_2 concentration.

<i>Sampling time</i>	<i>Calculated concentration (ppm)</i>	<i>Measured concentration (ppm)</i>	<i>Difference (ppm)</i>
20-09-94 13:12	375.7	375.5	0.2
20-09-94 17:30	366.5	366.8	-0.3
20-09-94 21:12	372.3	372.7	-0.4
21-09-94 1:13	377.4	377.1	0.3
21-09-94 5:18	368.2	369.5	-1.3
21-09-94 9:11	365.4	366.3	-0.9
21-09-94 13:13	357.8	357.8	0.0
21-09-94 17:14	361.2	361.6	-0.4
21-09-94 21:10	373.0	371.8	1.2
22-09-94 1:14	417.8	414.2	3.6
22-09-94 5:13	441.5	436.4	5.1

If the regional background concentration of CO_2 is known from measurements or can be assessed with adequate precision, the anthropogenic and biospheric contributions to the total CO_2 concentrations can be calculated as:

$$c_{\text{ant}} = ac_{\text{bg}}, \quad (14)$$

$$c_{\text{bio}} = bc_{\text{bg}}. \quad (15)$$

Equations (14) and (15) were tested using the data set from September 1994. Concentration

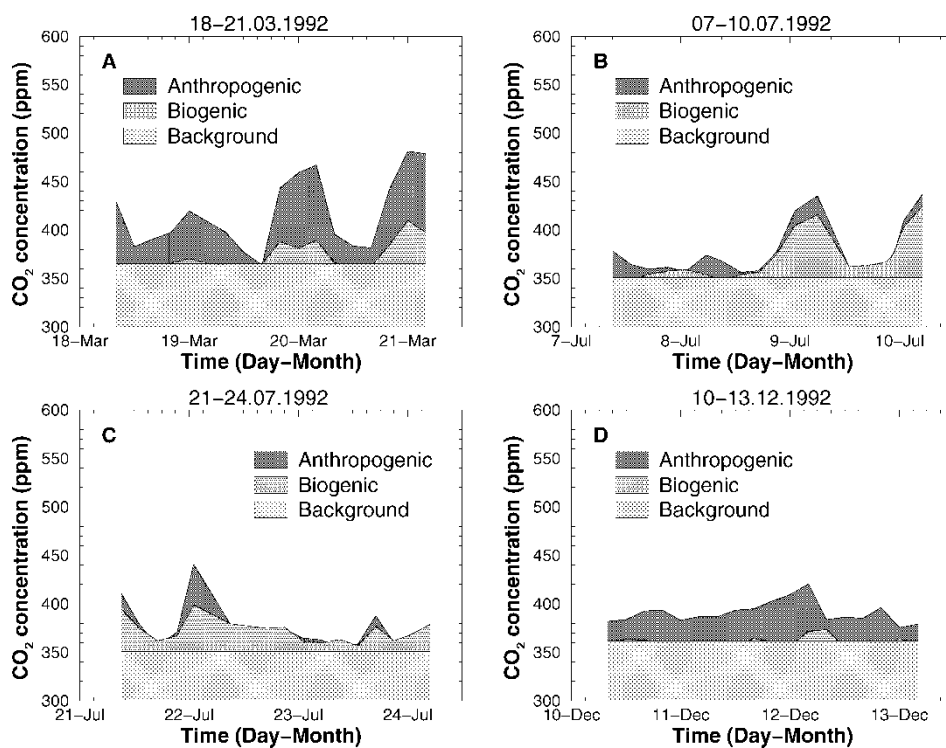


FIGURE 7 Model calculations of contribution of the background, biogenic and anthropogenic sources to atmospheric carbon dioxide concentration (March, July and December 1992).

data were calculated from the isotope measurements and compared with the concentration measurements (Tab. II). The agreement between measured and calculated data was very good. The difference is typically less than or around 1 ppm with a maximum difference of 5 ppm at the highest concentration.

The contributions c_{ant} and c_{bio} calculated using Eqs. (14) and (15) for the data obtained in 1992 are shown in Figure 7(A)–(D). It is clear from Figure 7 that during summertime in Krakow the dominant source of CO₂ is the local biosphere. The contribution of biospheric CO₂ reaches in our experiments up to 74 ppm during the night. The anthropogenic component is dominating during winter and early springtime and may reach up to 80 ppm, with a mean value of about 30 ppm. The second experiment done in July 1992 (Fig. 7(B)) shows the influence of rainfall on the behaviour of local fluxes. During the first night (after rain), we observe a much smaller flux from biogenic sources. One possible explanation can be the saturation of soil by rain water causing a depression of the soil CO₂ flux. This is also reflected in the correlation between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (Fig. 5(B)). Another factor affecting the results was the change in the air mass origin and circulation observed at back trajectories calculations. This might completely change the oxygen isotopic background conditions. As was mentioned above, the change of the oxygen isotopic composition of background CO₂ by 1‰ leads to a change in the calculated concentration by 50 ppm, which is the same order of magnitude as expected from local signals.

CONCLUSIONS

The results presented in the article revealed a relatively large variability of the isotopic composition and concentration of CO₂ on the diurnal time scale, particularly during summer. The change of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ between midday and midnight reached up to 4‰ and the concentration varied by up to 100 ppm. During winter the results are generally more stable.

The three-component mixing model proposed in this article allows us to separate contributions to the local CO₂ level originating from anthropogenic and biospheric emissions. Sensitivity calculations indicate that the derived contributions are highly sensitive on the actual characteristics (concentration and isotopic composition) of the background CO₂ component. This fact limits the use of this model to relatively short periods with stable meteorological conditions (no change in isotope characteristics of the background component).

Calculations show that even in an urban environment, the dominant contribution to the local CO₂ level during summertime is the biosphere, causing the concentration to increase in some cases up to 100 ppm during the night. A small anthropogenic flux of CO₂ is also observed, caused most probably by car traffic. In wintertime, the dominating source of local CO₂ is anthropogenic emission (house heating systems) while the biogenic component from respiration and biomass decomposition is negligible. The calculated mean contribution of anthropogenic CO₂ to the city atmosphere during winter is about 30 ppm, which is consistent with values derived from radiocarbon data [22, 23]. Though concentration data naturally add some more information to a given data set, we could show that only small errors are made (as compared to the observed signal and the natural variation) if we use only stable isotope measurements and a set of reasonable assumptions.

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APPENDIX – DETAILED DERIVATIONS OF EQS. (9)–(13)

If we express the biogenic (b) and anthropogenic (a) component as a fraction of the background CO₂ concentration, the following isotope mass balance equations can be formulated:

$$(1 + a + b)\delta^{13}\text{C}_{\text{tot}} = \delta^{13}\text{C}_{\text{bg}} + a\delta^{13}\text{C}_{\text{ant}} + b\delta^{13}\text{C}_{\text{bio}}, \quad (7)$$

$$(1 + a + b)\delta^{18}\text{O}_{\text{tot}} = \delta^{18}\text{O}_{\text{bg}} + a\delta^{18}\text{O}_{\text{ant}} + b\delta^{18}\text{O}_{\text{bio}}. \quad (8)$$

From Eqs. (7) and (8):

$$\delta^{13}\text{C}_{\text{tot}} = \frac{\delta^{13}\text{C}_{\text{bg}} + a\delta^{13}\text{C}_{\text{ant}} + b\delta^{13}\text{C}_{\text{bio}}}{(1 + a + b)}, \quad (7a)$$

$$\delta^{18}\text{O}_{\text{tot}} = \frac{\delta^{18}\text{O}_{\text{bg}} + a\delta^{18}\text{O}_{\text{ant}} + b\delta^{18}\text{O}_{\text{bio}}}{(1 + a + b)}. \quad (8a)$$

The interpretation of the data sets containing no concentration data can be done using the regression coefficient (A) between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$. Using Eqs. (7a) and (8a) one can derive a formula describing that coefficient:

$$A = \frac{\delta^{18}\text{O}_{\text{tot}} - \delta^{18}\text{O}_{\text{bg}}}{\delta^{13}\text{C}_{\text{tot}} - \delta^{13}\text{C}_{\text{bg}}}. \quad (9)$$

Next some transformations:

$$A = \frac{((\delta^{18}\text{O}_{\text{bg}} + a\delta^{18}\text{O}_{\text{ant}} + b\delta^{18}\text{O}_{\text{bio}})/(1 + a + b)) - \delta^{18}\text{O}_{\text{bg}}}{((\delta^{13}\text{C}_{\text{bg}} + a\delta^{13}\text{C}_{\text{ant}} + b\delta^{13}\text{C}_{\text{bio}})/(1 + a + b)) - \delta^{13}\text{C}_{\text{bg}}}, \quad (9a)$$

$$A = \frac{((\delta^{18}\text{O}_{\text{bg}} + a\delta^{18}\text{O}_{\text{ant}} + b\delta^{18}\text{O}_{\text{bio}} - (1 + a + b)\delta^{18}\text{O}_{\text{bg}})/(1 + a + b))}{((\delta^{13}\text{C}_{\text{bg}} + a\delta^{13}\text{C}_{\text{ant}} + b\delta^{13}\text{C}_{\text{bio}} - (1 + a + b)\delta^{13}\text{C}_{\text{bg}})/(1 + a + b))}, \quad (9b)$$

$$A = \frac{\delta^{18}\text{O}_{\text{bg}} + a\delta^{18}\text{O}_{\text{ant}} + b\delta^{18}\text{O}_{\text{bio}} - (1 + a + b)\delta^{18}\text{O}_{\text{bg}}}{\delta^{13}\text{C}_{\text{bg}} + a\delta^{13}\text{C}_{\text{ant}} + b\delta^{13}\text{C}_{\text{bio}} - (1 + a + b)\delta^{13}\text{C}_{\text{bg}}}, \quad (9c)$$

$$A = \frac{a(\delta^{18}\text{O}_{\text{ant}} - \delta^{18}\text{O}_{\text{bg}}) + b(\delta^{18}\text{O}_{\text{bio}} - \delta^{18}\text{O}_{\text{bg}})}{a(\delta^{13}\text{C}_{\text{ant}} - \delta^{13}\text{C}_{\text{bg}}) + b(\delta^{13}\text{C}_{\text{bio}} - \delta^{13}\text{C}_{\text{bg}})}, \quad (9d)$$

$$A = \frac{(a/b)(\delta^{18}\text{O}_{\text{ant}} - \delta^{18}\text{O}_{\text{bg}}) + (\delta^{18}\text{O}_{\text{bio}} - \delta^{18}\text{O}_{\text{bg}})}{(a/b)(\delta^{13}\text{C}_{\text{ant}} - \delta^{13}\text{C}_{\text{bg}}) + (\delta^{13}\text{C}_{\text{bio}} - \delta^{13}\text{C}_{\text{bg}})}, \quad (10)$$

$$A \left(\frac{a}{b} (\delta^{13}\text{C}_{\text{ant}} - \delta^{13}\text{C}_{\text{bg}}) + (\delta^{13}\text{C}_{\text{bio}} - \delta^{13}\text{C}_{\text{bg}}) \right) = \frac{a}{b} (\delta^{18}\text{O}_{\text{ant}} - \delta^{18}\text{O}_{\text{bg}}) + (\delta^{18}\text{O}_{\text{bio}} - \delta^{18}\text{O}_{\text{bg}}), \quad (10a)$$

$$A \frac{a}{b} (\delta^{13}\text{C}_{\text{ant}} - \delta^{13}\text{C}_{\text{bg}}) - \frac{a}{b} (\delta^{18}\text{O}_{\text{ant}} - \delta^{18}\text{O}_{\text{bg}}) = (\delta^{18}\text{O}_{\text{bio}} - \delta^{18}\text{O}_{\text{bg}}) - A (\delta^{13}\text{C}_{\text{bio}} - \delta^{13}\text{C}_{\text{bg}}), \quad (10b)$$

$$\frac{a}{b} (A (\delta^{13}\text{C}_{\text{ant}} - \delta^{13}\text{C}_{\text{bg}}) - (\delta^{18}\text{O}_{\text{ant}} - \delta^{18}\text{O}_{\text{bg}})) = (\delta^{18}\text{O}_{\text{bio}} - \delta^{18}\text{O}_{\text{bg}}) - A (\delta^{13}\text{C}_{\text{bio}} - \delta^{13}\text{C}_{\text{bg}}), \quad (10c)$$

$$\frac{a}{b} = \frac{(\delta^{18}\text{O}_{\text{bio}} - \delta^{18}\text{O}_{\text{bg}}) - A (\delta^{13}\text{C}_{\text{bio}} - \delta^{13}\text{C}_{\text{bg}})}{A (\delta^{13}\text{C}_{\text{ant}} - \delta^{13}\text{C}_{\text{bg}}) - (\delta^{18}\text{O}_{\text{ant}} - \delta^{18}\text{O}_{\text{bg}})}, \quad (10d)$$

Extending Eq. (10d) by multiplication with $(\delta^{13}\text{C}_{\text{bio}} - \delta^{13}\text{C}_{\text{bg}})$ yields:

$$\frac{a}{b} = \frac{((\delta^{18}\text{O}_{\text{bio}} - \delta^{18}\text{O}_{\text{bg}}) / (\delta^{13}\text{C}_{\text{bio}} - \delta^{13}\text{C}_{\text{bg}})) - (A (\delta^{13}\text{C}_{\text{bio}} - \delta^{13}\text{C}_{\text{bg}}) / (\delta^{13}\text{C}_{\text{bio}} - \delta^{13}\text{C}_{\text{bg}})) \times (\delta^{13}\text{C}_{\text{bio}} - \delta^{13}\text{C}_{\text{bg}})}{(A (\delta^{13}\text{C}_{\text{ant}} - \delta^{13}\text{C}_{\text{bg}}) / (\delta^{13}\text{C}_{\text{ant}} - \delta^{13}\text{C}_{\text{bg}})) - ((\delta^{18}\text{O}_{\text{ant}} - \delta^{18}\text{O}_{\text{bg}}) / (\delta^{13}\text{C}_{\text{ant}} - \delta^{13}\text{C}_{\text{bg}})) \times (\delta^{13}\text{C}_{\text{ant}} - \delta^{13}\text{C}_{\text{bg}})}. \quad (10e)$$

In situations when 100% of the local CO_2 contribution is of biogenic origin, the slope A_{bio} of the linear fit of the ^{18}O and ^{13}C data (two-component mixing) can be expressed by the following equation:

$$A_{\text{bio}} = \frac{\delta^{18}\text{O}_{\text{bio}} - \delta^{18}\text{O}_{\text{bg}}}{\delta^{13}\text{C}_{\text{bio}} - \delta^{13}\text{C}_{\text{bg}}}. \quad (11)$$

where values with subscript ‘bio’ and ‘bg’ represent the measured (assessed) isotopic composition of the local biogenic CO_2 and background CO_2 , respectively. If the contribution is solely of anthropogenic origin, the corresponding equation for A_{ant} will have the following form:

$$A_{\text{ant}} = \frac{\delta^{18}\text{O}_{\text{ant}} - \delta^{18}\text{O}_{\text{bg}}}{\delta^{13}\text{C}_{\text{ant}} - \delta^{13}\text{C}_{\text{bg}}}, \quad (12)$$

where values with subscript ‘ant’ and ‘bg’ represent the measured (assessed) isotopic composition of the local anthropogenic CO_2 and background CO_2 , respectively.

Combining Eqs. (10e), (11) and (12), one can obtain the following expression for the ratio a/b representing the relative proportion of the anthropogenic and biogenic component in the sampled atmospheric CO_2 :

$$\frac{a}{b} = \frac{A_{\text{bio}} - A}{A - A_{\text{ant}}} \times \frac{\delta^{13}\text{C}_{\text{bio}} - \delta^{13}\text{C}_{\text{bg}}}{\delta^{13}\text{C}_{\text{ant}} - \delta^{13}\text{C}_{\text{bg}}}. \quad (13)$$